NORMAL ALKANES AT PLATINUM ANODES

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Extensive work on direct hydrocarbon cells has shown the normal alkanes to be the most suitable family of fuels (1). How their performance changes with molecular weight has consequently become important. The most straightforward way of establishing this relationship is by measuring for an anode (or similar anodes) under conditions intended to be identical the steady-state current densities supported by the several homologues at fixed anodic overvoltage. The anodic overvoltage η_a is usually measured as the potential difference E_{A-R} between the working anode and a reversible hydrogen reference electrode in the same cell. Figure 1 shows the results of an early comprehensive study of this kind.(1a,b)

A plot like Figure 1 is adequate as a record of experimental results or as a basis for comparing results for a single fuel. But when comparisons that involve more than one fuel are to be made, one must remember that each alkane (or other fuel) can surrender a different number, n_e, of electrons per molecule upon anodic oxidation. Experiment has shown that the normal alkanes are often completely oxidized, yielding H^+ and CO_2 at fuel-cell anodes(2,a,b,c). When this is true, $n_e = 6n + 2$ for the n'th member of the homologues series of normal alkanes.

Current densities like those in Figure 1 will be expressed in molecular units (further specification unnecessary)* if each of them is divided by the value of n_e for the corresponding normal alkane. When this is done (Figure 2), the maxima in Figure 1 disappear, and methane takes its place as the fuel of highest molecular performance. We have similarly transformed data by Binder and co-workers(2b), and by Cairns(2c) with the results in Figures 3, 4, and 5. Figure 3 is in accord with Figure 2; in the other figures, methane fails to achieve top performance to a degree that increases with E_{A-R} and with current density. (E_{A-R} and i increase together in this range.)

The experimental conditions under which the presumed steady-state current densities were measured varied so widely that they will not be discussed. The experimental conditions most nearly certain to have given true steady-state current densities are those of Binder and co-workers. Only here were all fuels at a known identical pressure, 1.5 atm. The gases at this pressure flowed through an anode heavily loaded (180 mg/cm^2) with Raney platinum; unreacted fuel and carbon dioxide(2b) bubbled through the electrolyte, 3N H_2SO_4 at 100°C. The first reading was taken after 24 hours, and subsequent readings at 2-hour intervals. These data consequently provide the best test of whether the maxima in performance curves disappear when they are placed on a molecular basis. Comparison of Figure 3 with Figure 5

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*With 10^5 coulombs as the Faraday, and with current density in ma/cm^2, the current density in molecular units (i/n_e) is 10^8 times the moles fuel/sec oxidized on 1 cm^2 of electrode surface. The number of electrons per molecule, n_e, yielded up by the fuel during oxidation is of course equal to the experimental number of Faradays for a mole of fuel. When the anodic reactions are complex, n_e may be only an average value.

of Reference 2b shows that the test was successfully passed.

A hydrocarbon anode at a steady state is a complex system in which various consecutive processes (physical, chemical, electro-chemical) proceed at the same absolute rate. No one process is therefore rate-determining, although the rate constants associated with each process help establish the absolute steady-state rate of all. Reliable data for the detailed analysis of such steady states do not exist.

Attempts to interpret current densities as rates in terms of overvoltages usually founder because one cannot establish the con-tributions that the individual processes make to the measured over-voltage. "Tafel plots" for the data of Figures 1 and 2 appear in Figures 6 and 7. Clearly, these plots are not straight lines, and this testifies to the complex and composite character of the mea-sured overvoltage. Figure 7 is tidier than Figure 6, which supports the "molecular units" as more rational that ma/cm^2. Note, especially in Figure 7, that increasing anodic overvoltage increases current density more markedly at intermediate values of n: the plots for CH_4 and for $C_{16}H_{34}$ resemble each other. Evidence too extensive for discussion here (3,4) has shown that methane is adsorbed more slowly on platinum than are its homologues, and that the oxygenation pro-cess on the anode (which leads ultimately to CO_2) is simplest for methane. For the first fact, the symmetry of methane may be re-sponsible; and the absence of C-C bonds is responsible for the second. The gain in performance occruing to methane from the second fact appears to override any loss from the first. The greater effect of increasing overvoltage on current density for the higher homo-logues can be explained as resulting from accelerations in the rates of breaking carbon-carbon bonds, and in the rates of other reactions that rid the anode of dehydrogenated alkane residues.

Though Tafel slopes cannot of themselves establish mechanism, we must admit the possibility that similarities in Tafel plots, such as that between the plots for CH_4 and $C_{16}H_{34}$, point to similarities in the mechanism for anodic oxidation. For example, such a possi-bility is that cetane, being a large molecule, is held by the sur-face only at isolated points where anodic oxidation occurs (as for methane) without the breaking of carbon-carbon bonds and perhaps with desorption of incompletely oxidized molecules. Note, however, that complete oxidation to CO_2 has been shown by Grubb and Michalske (unpublished) to occur within experimental error for the normal alkanes up to and including octane. The suggestion just made for higher alkanes needs to be tested experimentally, and it serves as a reminder that $n_e = 6n + 2$ cannot always be taken for granted.

We shall use current densities in molecular units in comparing the reforming of methane before it reaches the anode with its direct oxidation at the anode. We make this comparison on the basis of the endothermic reaction

$$CH_4 + H_2O = CO + 3H_2 \qquad (1)$$
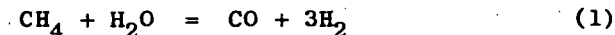
At an overvoltage of 0.3 volt, observed current densities under the conditions of Figure 1 are: CH_4, 13.2 ma/cm^2; CO, 58 ma/cm^2; H_2, >500 ma/cm^2. Expressed in molecular units, these current densities become CH_4, 1.65; CO, 29; H_2, >250. The attractiveness of reforming, from a kinetic point of view, is enhanced when current densities are expressed in molecular units.

We wish to thank Dr. L.W. Niedrach for providing us with the CO datum used above.

We shall not claim that the current density in molecular units is always to be preferred in comparing performances of different fuels or in judging the effectiveness of electrocatalysts. But we do wish to point out the advantages of basing current densities upon the molecule - especially when the anode process is as complex as the steady state at the hydrocarbon anode, which was alluded to above. In the series of consecutive processes that proceed at the steady-state rate on this anode, the first are probably transport processes, and they are known to involve the molecule. After these come the processes (e.g., dissociative adsorption, electron transfer, breaking of bonds, oxygenation) that take place on the anode surfaces. These processes are unknown in number and involve unknown intermediate species. Because one (or at most two) electrons are transferred in a single process, the number of processes in which electron transfer occurs will vary from one alkane to another as n_e varies. By basing comparisons on the current density in ma/cm^2 (or similar units), we base the comparison on the integrated contribution of all electron-transfer processes, the nature and number of which vary from one alkane to another. We hope that current densities in molecular units will be used by others as a basis for comparing the anodic performances of different fuels so that the usefulness of these units can soon be decided.

SUMMARY

1. Current densities in molecular units as opposed to, say, ma/cm^2, are logical for comparing the performance of the various normal alkanes at hydrocarbon anodes. The statement holds also for other cases.

2. Current densities being expressed in molecular units, methane outperforms other normal alkanes at fuel-cell anodes under certain steady-state conditions with sulfuric and phosphoric acid as electrolytes. With electrolytes containing hydrofluoric acid, the statement does not hold. Further work is needed, but the absence of carbon-carbon bonds in methane strongly supports the idea that it ranks first in anodic reactivity among normal alkanes.

3. It is possible that heavy alkanes, such as cetane, are oxidized incompletely at anodes and without the rupture of carbon-carbon bonds, which would cause their (partial) anodic oxidation to resemble somewhat the anodic oxidation of methane. Further work is needed.

4. Current densities in molecular units need and deserve further testing as a basis for comparing the performance of different fuels at fuel-cell anodes.

REFERENCES

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   (b) Fig. 1, which completes the publication of performance results by Grubb and Michalske.
2. (a) Grubb, W.T. and Michalske, C.J., J. Electrochem. Soc., 111, 1015 (1964).

(b) Binder, H., Kohling, A., Krupp, H., Richter, K., and Sandstede, G., *ibid.*, 112, 355 (1965).
(c) Cairns, E.J., *ibid.*, 113, 1203 (1966).

3. Niedrach, L.W., *ibid.*, 113, 645 (1966).

4. Gilman, S. in *Hydrocarbon Fuel Cell Technology*, B.S. Baker, Ed., Academic Press, New York, N.Y. (1965), p.349.
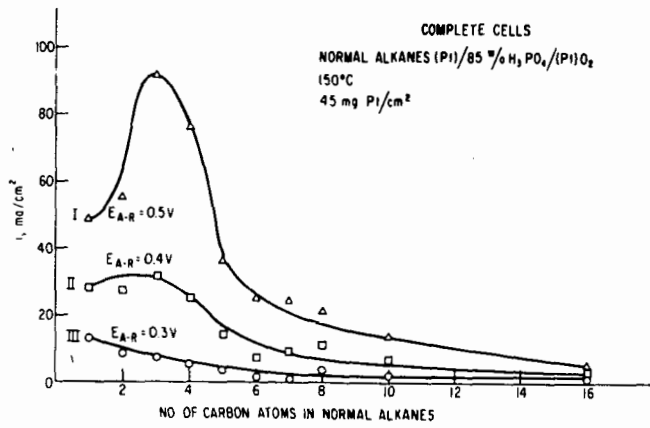
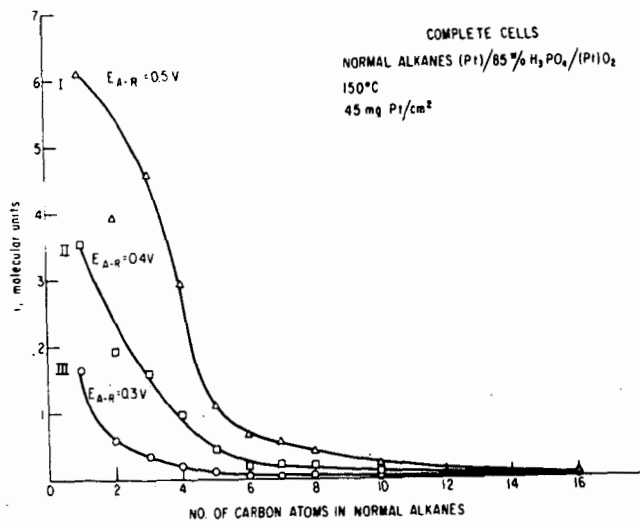Figure 1.   Performance of normal alkanes as fuels.[1]

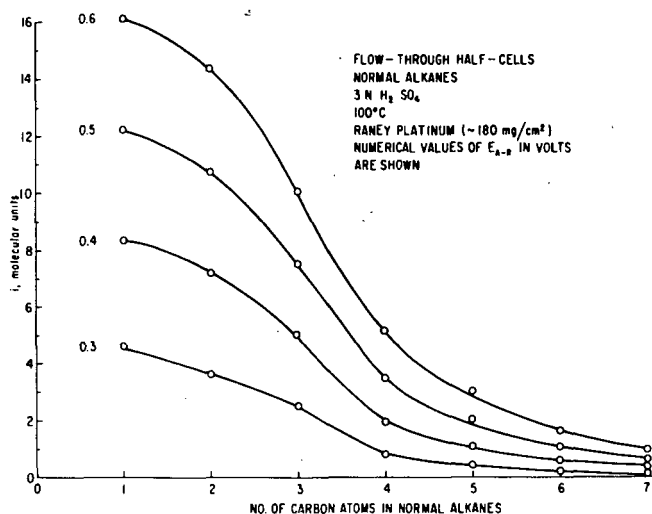Figure 2.   Performance data of Figure 1 in molecular units.
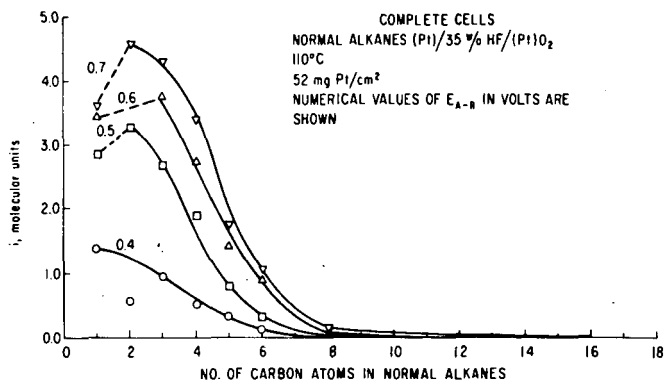
Figure 3. Performance data of Reference 2b in molecular units.

Figure 4. Performance data from Reference 2c in molecular units.
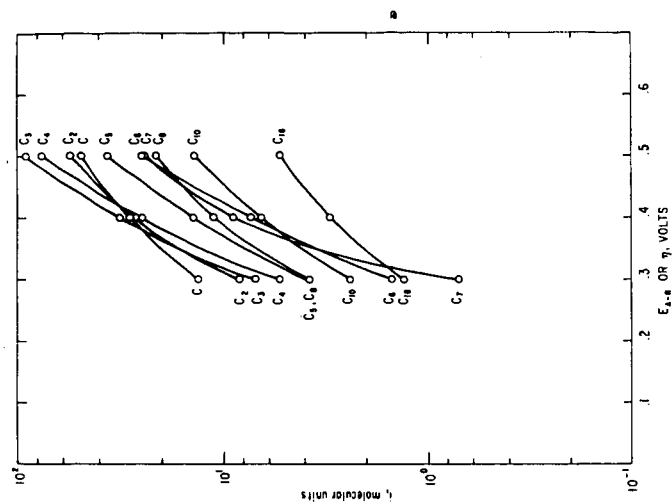
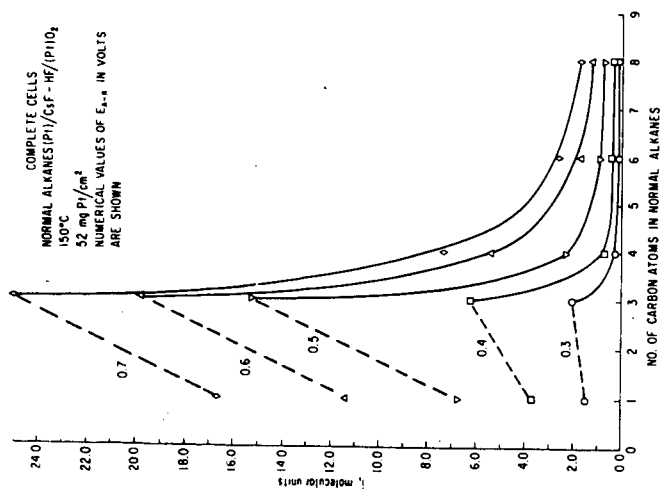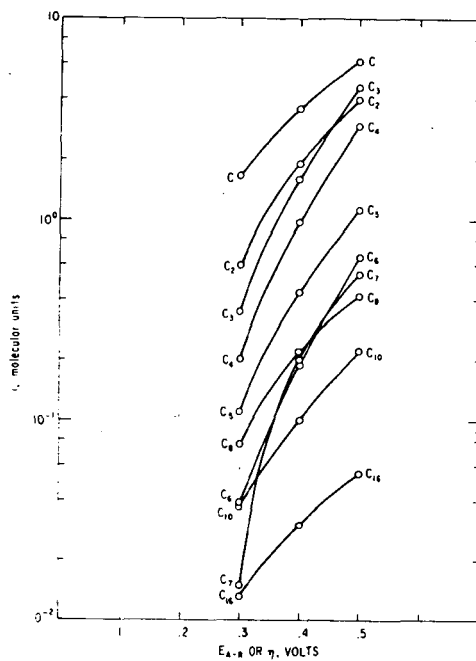Figure 6. Tafel plots for Figure 1.

Figure 5. Performance data from Reference 2c in molecular units.

Figure 7.   Tafel plots for Figure 2.